

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE THE APPLICATION OF: HAYASHI, ET AL.

APPLICATION NO.: 10/561,830

FILLING DATE: DECEMBER 22, 2005

GROUP ART UNIT: 1795

EXAMINER: EOFF, ANCA

TITLE: POSITIVE RESIST COMPOSITION AND METHOD OF FORMING
RESIST PATTERN USING SAME

DECLARATION UNDER 37 C.F.R. § 1.132

Commissioner for Patents

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Alexandria, VA 22313-1450

Sir:

I, Hideo HADA, do hereby declare that:

I have been an employee of Tokyo Ohka Kogyo Co., Ltd., Japan, the assignee of the above-identified United States patent application, since April 1, 1994, being engaged in research and development work relating to resist compositions and other related products of the company.

Although I am not one of the applicants of the above-identified application, I have full knowledge of the subject matter of the above-identified application.

I carried out experiments to demonstrate the unexpected advantages obtained by the use of the structural unit (a4) and the structural unit (a5) recited in claim 17 of the present application, and the criticality of the molar percent range of the structural unit (a4) recited in claim 17 of the present application.

I have a good knowledge of the English language and have read and understood the application papers and the prosecution history of this and the antecedent applications as well as the Examiner's references cited therein.

PURPOSE, METHOD AND RESULTS

(1) Purpose of the Experiments:

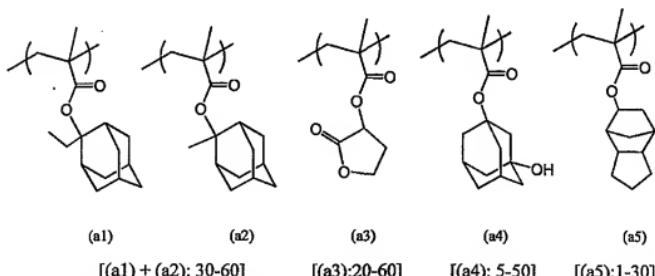
The purpose of the Experiments described in this declaration is to demonstrate the unexpected advantages obtained by the use of the structural unit (a4) and the structural unit (a5) recited in claim 17 of the present application, and the criticality of the molar percent range of the structural unit (a4) recited in claim 17 of the present application.

(2) Method and Results of Experiments:

Method:

(i) Production of polymers

Each of the polymers (A)-1 to (A)-4 and (A)-1' to (A)-3' having structural units with the molar ratio indicated in Table A was synthesized. The molar ratio of the respective structural units was determined by carbon 13 nuclear magnetic resonance spectroscopy (600MHz $^{13}\text{C-NMR}$). Further, the weight average molecular weight (M_w) and the dispersity (M_w/M_n) of the obtained polymers were determined by the polystyrene equivalent value as measured by gel permeation chromatography (GPC).



*Values in brackets indicate the molar percent range recited in claim 17 of the present application

Table A

Polymer	(a1)	(a2)	(a3)	(a4)	(a5)	Mw
(A)-1	20	10	20	45	5	9,500
(A)-2	25	20	35	5	15	8,200
(A)-3	25	10	20	40	5	9,000
(A)-4	25	20	25	5	25	8,700
(A)-1'	25	20	40	-	15	6,600
(A)-2'	20	10	10	55	5	8,200
(A)-3'	25	10	20	45	-	7,400

(ii) Production of resist compositions

The components shown in Table B were mixed together and dissolved to obtain resist compositions. In the compositions, the reason why the amounts of component (C)-2 (γ -butyrolactone) are different is that the solubility of each polymer in a solvent is different, and it was necessary to adjust the amount of γ -butyrolactone to dissolve the polymers.

Table B

	Component (A)	Component (B)	Component (D)	Component (C)
Test Example 1	(A)-1 [100]	(B)-1 [3.0]	(D)-1 [0.2]	(C)-1 [1000] (C)-2 [100]
Test Example 2	(A)-2 [100]	(B)-1 [3.0]	(D)-1 [0.2]	(C)-1 [1000] (C)-2 [25]
Test Example 3	(A)-3 [100]	(B)-1 [3.0]	(D)-1 [0.2]	(C)-1 [1000] (C)-2 [25]
Test Example 4	(A)-4 [100]	(B)-1 [3.0]	(D)-1 [0.2]	(C)-1 [1000] (C)-2 [25]
Comparative Test Example 1	(A)-1' [100]	(B)-1 [3.0]	(D)-1 [0.2]	(C)-1 [1000] (C)-2 [25]
Comparative Test Example 2	(A)-2' [100]	(B)-1 [3.0]	(D)-1 [0.2]	(C)-1 [1000] (C)-2 [100*]
Comparative Test Example 3	(A)-3' [100]	(B)-1 [3.0]	(D)-1 [0.2]	(C)-1 [1000] (C)-2 [100]

*In Comparative Test Example 2 using polymer (A)-2' containing 55 mol% of the structural unit (a4), the polymer could not be dissolved in the component (C) even when the amount of (C)-2 (γ -butyrolactone) was increased to 500 parts by weight.

In Table B, the reference characters indicate the following. Further, the values in brackets [] indicate the amount (in terms of parts by weight) of the component added.

- (A)-1: aforementioned polymer (A)-1
- (A)-2: aforementioned polymer (A)-2
- (A)-3: aforementioned polymer (A)-3
- (A)-4: aforementioned polymer (A)-4
- (A)-1': aforementioned polymer (A)-1'
- (A)-2': aforementioned polymer (A)-2'
- (A)-3': aforementioned polymer (A)-3'
- (B)-1: triphenylsulfonium nonafluorobutanesulfonate
- (C)-1: propylene glycol monomethyl ether acetate (PGMEA)
- (C)-2: γ -butyrolactone
- (D)-1: triethanolamine

(iii) Formation of resist pattern

An organic anti-reflection film composition (product name: ARC29, manufactured by Brewer Science Ltd.) was applied to an 8-inch silicon wafer using a coating apparatus ACT8 (manufactured by Tokyo Electron Limited), and the composition was then baked at 205°C for 60 seconds on a hot plate, thereby forming an organic anti-reflection film having a film thickness of 77 nm. Then, each of the resist compositions of the Test Examples and Comparative Test Examples excluding Comparative Test Example 2 was applied to the anti-reflection film using a spinner, and was then prebaked (PAB) on a hotplate at 110°C for 90 seconds and dried, thereby forming a resist film having a film thickness of 300 nm.

Subsequently, using an ArF exposure apparatus NSR-S302A (manufactured by Nikon Corporation, NA (numerical aperture) = 0.60, σ = 0.75), the resist film was selectively irradiated with an ArF excimer laser (193 nm) through a mask pattern. The irradiation was performed while fixing the focus, and 50 shots were conducted at intervals of 1 mJ/cm² over a range of 5.0 to 54.0 mJ/cm².

Thereafter, a post exposure bake (PEB) treatment was conducted at 110°C for 90 seconds, followed by paddle development for 60 seconds at 23°C in a 2.38% by weight aqueous solution of tetramethylammonium hydroxide, followed by washing with water for 20 seconds and drying, thereby obtaining a resist pattern.

With respect to an isolated line and space pattern targeting a line width of 120 nm and a pitch of 1,320 nm, the result of each exposure shot was observed by a scanning electron microscope. The line width closest to 120 nm and the exposure dose for achieving that line width are shown in Table C. A line width closer to 120 nm indicates a better result. In Table C, the results of the Test Examples and Comparative Examples are shown in descending order of the absolute value of the difference between the target size and the actual size.

Table C

	(a1)	(a2)	(a3)	(a4)	(a5)	Exposure dose (mJ/cm ²)	Line width of Iso pattern (nm)	Difference between target size and actual size (Absolute value)
Comparative Test Example 1	25	20	40	-	15	-	No pattern	-
Comparative Test Example 2	20	10	10	55	5	-	(Polymer could not be dissolved)	-
Comparative Test Example 3	25	10	20	45	-	14.0	150.6	30.6
Test Example 2	25	20	35	5	15	5.0	148.5	28.5
Test Example 4	25	20	25	5	25	6.0	100.7	19.3
Test Example 3	25	10	20	40	5	10.0	135.9	15.9
Test Example 1	20	10	20	45	5	22.0	124.6	4.6

Results:

As seen from the results, in Test Examples 1 to 4 in which a polymer containing all of the structural units (a1), (a2), (a3), (a4) and (a5), and the amount of the structural unit (a4) is in the range of 5 to 50 mol% was used, excellent results were achieved, as compared to Comparative Test Examples 1 to 3. Especially in Test Examples 2 and 4, although the amount of the structural unit (a4) was the same as the lower limit of the range recited in claim 17 of the present application (i.e., 5 mol%), excellent results could be achieved. These results indicate that the lower limit of the molar percent range of the structural unit (a4) recited in claim 17 gives practical meaning of using the structural unit (a4).

On the other hand, in Comparative Test Example 1 in which the polymer contained no structural unit (a4), a pattern could not be formed.

In Comparative Test Example 3 in which the polymer contained no structural unit (a5), the difference between the target size and the actual size was larger than those in Test Examples 1 to 4.

In Comparative Test Example 2 in which the polymer contained all of the structural units (a1), (a2), (a3), (a4) and (a5) but the amount of the structural unit (a4) exceeded 50 mol%, the solubility of the polymer was so poor that the polymer could

not be dissolved in the component (C).

(3) Conclusion

From the results of the experiments, it can be fairly concluded that a resist composition containing a polymer which includes all of the structural units (a1), (a2), (a3), (a4) and (a5) exhibit advantageous lithography properties over resist compositions containing a polymer which lacks the structural unit (a4) or the structural unit (a5). Further, it can be fairly concluded that the molar percent range of the structural unit (a4) (5 to 50 mol%) recited in claim 17 is critical for achieving excellent lithography properties.

Appl. No. 10/561,830
Filed: December 22, 2005

I further declare that all statements made herein to our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Hideo Hada

Signature (Hideo HADA)

November 26, 2009

Date